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13. ABSTRACT *(Maximum 200 words)*

Intense red emission peaking at 703 mm was observed when a heated metal wire was placed downstream of an $O_2(^1\Delta_g)$ generator used in the chemical oxygen iodine laser (COIL) system. The $O_2(^1\Delta_g)$ is produced by bubbling Cl_2 through an alkaline solution of H_2O_2. Evidence has been found that this strong red emission requires the presence of both $O_2(^1\Delta_g)$ and Cl_2 in contact with a heated metal surface. Several metals have been used. The red emission spectrum is independent of the metal and the intensity is strongest for copper. An attempt was made to observe laser action but no gain was detected. The identity of the species responsible for the strong red emission has not been established.

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SURFACE-CATALYZED CHEMILUMINESCENCE

Beginning with the pioneering work of Kasper and Pimentel [1] in 1964, there has been much interest in the production of chemical lasers, particularly those operating in the visible. Presently, the shortest wavelength high energy chemical laser is the chemical oxygen iodine laser (COIL), operating at 1.315 μm on the $^2P_{1/2} \rightarrow {}^2P_{3/2}$ transition in atomic iodine [2,3]. The excited iodine atoms are produced by resonant energy transfer from $O_2(^1\Delta_g)$, which is generated by the overall reaction

$$Cl_2(g) + H_2O_2(l) + 2KOH(l) \rightarrow O_2(^1\Delta_g) + 2KCl + 2H_2O \qquad (1)$$

In 1989, Yoshida *et al.* [4] reported a new visible chemical laser using a subsonic COIL system. They claimed that "so-called dimol emission of singlet oxygen could be enormously intensified" by injecting iodine vapor downstream of the $O_2(^1\Delta_g)$ reactor. The emission was attributed to $O_2(^1\Delta_g) \cdot O_2(^1\Delta_g) \rightarrow O_2(^3\Sigma_g^-, v = 0) + O_2(^3\Sigma_g^-, v = 1)$. A gain of 2.8% was measured at 703 nm [5]. However, the red emission did not show the two characteristic bands of dimol emission at 634 and 703 nm [6]. Recently, Yoshida, Tokuda and Shimizu [7] have revised their assignment of the emitter to be a stable excited O_4 molecule. Moreover, they report that injection of iodine is unnecessary to initiate the intense red glow. Instead, heating of the $O_2(^1\Delta_g)$ metal inlet (Al or Cu) suffices. Stimulated by these results, we have undertaken a simple study of what conditions affect the appearance and intensity of the 703 nm red emission.

Figure 1 shows the experimental apparatus. The $O_2(^1\Delta_g)$ molecules were generated by bubbling Cl_2 through a plexiglass cylinder containing an aqueous solution of H_2O_2 and KOH. The resulting stream of gas passed through a trap cooled by dry ice and ethanol (−78° C) to remove water vapor. The $O_2(^1\Delta_g)$ stream enters an optical cavity, 300 mm long by 200 mm wide by 45 mm high. A metal wire in the form of a coil was placed inside the optical cavity perpendicular to the stream. This coil having 6–8 turns per cm could be resistively heated during the experiment by a DC power supply attached to a variable transformer. Two windows (2″ in diameter) are attached to the optical cavity downstream of the coil of metal wire. In addition, the body of the cavity is constructed from plexiglass, allowing direct observation from above.

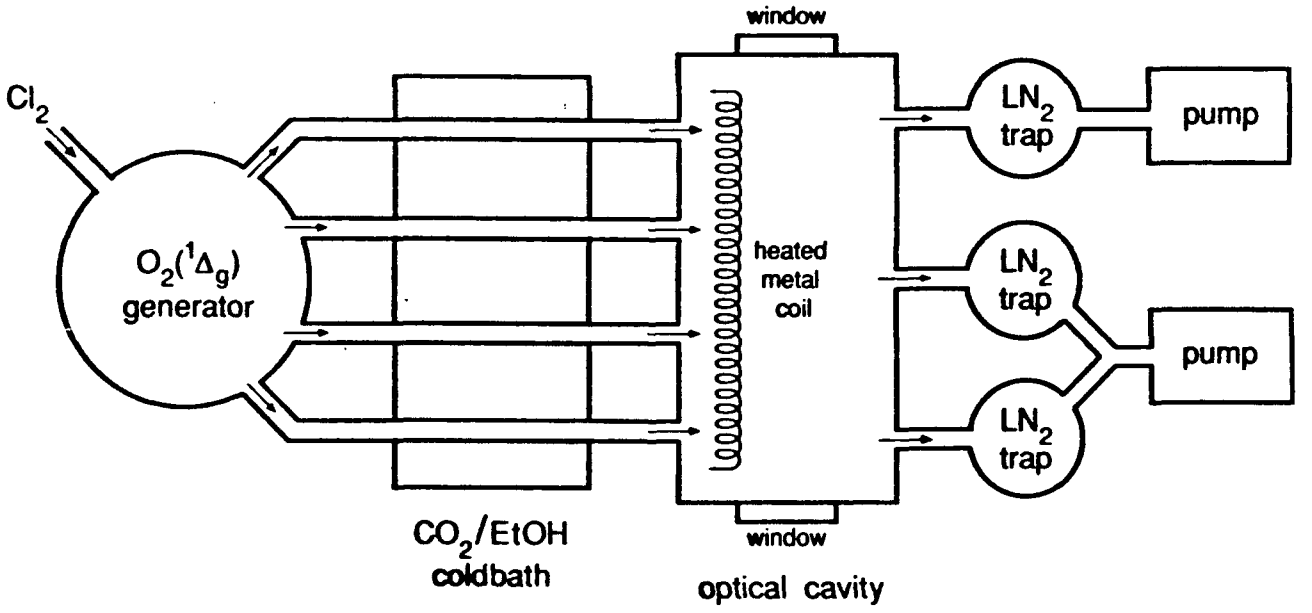

Fig. 1. Schematic drawing of the experimental setup for observing enhanced red emissions in the COIL laser system.

When the Cl_2 gas is allowed to flow into the $O_2(^1\Delta_g)$ generator but the wire coil is not heated, a faint red glow fills the optical cavity. This emission is thought to be dimol emission involving the collisions between two $O_2(^1\Delta_g)$ molecules [6]. Upon heating the wire to about 600 ± 50° C, as measured by a thermocouple, there is a strong enhancement of the red emission. This enhancement often is short-lived, lasting only for seconds. Increased heating does not restore the emission process, and the wires cannot be successfully reused. This enhancement takes place both upstream and downstream from the heated coil. The upstream region extends only 1–2 cm, while the downstream region is 15–20 cm long.

The following metals were tried: W, Ni, stainless steel, Pt, nichrome, Cu, and tin-coated Cu. Of these, only Cu and Sn-coated Cu gave enhanced emission that lasts for as long as there is $O_2(^1\Delta_g)$ generation. In addition, Cu and Sn-coated Cu gave the most intense emission (2000 times stronger than the background dimol emission) and could be reused. Evidently, the surfaces of the other metals become "poisoned."

A low-resolution emission spectrum was recorded using an optical multichannel analyzer (PAR OMA-1205A with OMA-1205D detector) attached to a 0.25-m polychromator. Figure 2 presents the resulting spectrums along with the detector response curve. This spectrum is basically identical (after correction for the response curve of the detector) with the spectrum shown in Fig. 2 of Yoshida, Tokuda, and Shimizu [7] and Fig. 4 of Yoshida *et al.* [4]. It peaks near 703 nm and shows partially resolved structure, particularly to the red of the peak. Because the emission spectrum does not change with the metal used in the heated coil, we conclude that the heated metal plays the role of a catalyst in producing the emitter responsible for the intense red glow.

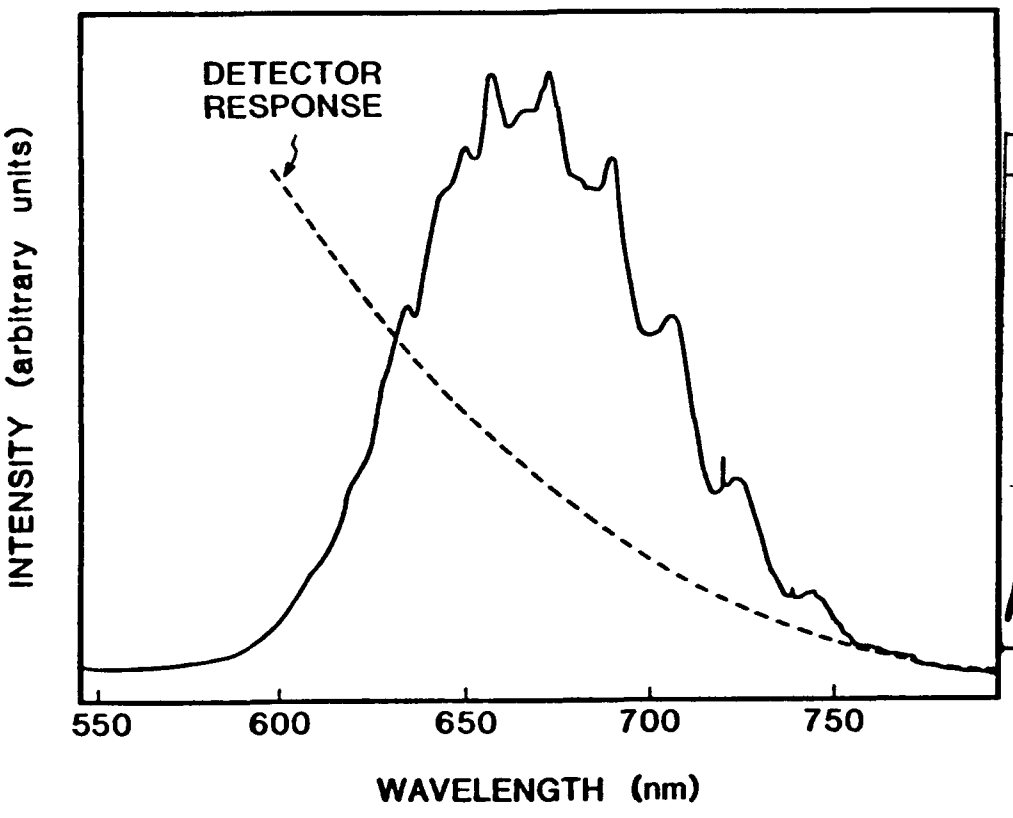

Fig. 2. Red emission feature taken under low resolution (5 nm) using an optical multichannel analyzer. This spectrum was recorded using a Sm-coated copper coil heated to 600 C in the singlet oxygen flow stream containing residual Cl_2.

We attempted to observe laser action by replacing the two windows in the optical cavity by a pair of 1-m concave mirrors. These mirrors have a broad-band dielectric coating (100 nm FWHW), centered at 703 nm (99.8% reflectivity, CVI). A photomultiplier (RCA 7265) was placed in front of one of the mirrors and fitted with a red bandpass filter centered at 700 nm (20 nm FWHM). A photodiode was placed so that it viewed the red glow perpendicular to the cavity axis. Using a two-pen chart recorder, measurements were made of the photomultiplier signal referenced to the photodiode signal when the laser cavity was aligned and unaligned. No significant differences were ever recorded, which indicates that there is no lasing action.

To learn more about the identity of the emitter responsible for the 703 nm band, we replaced the dry ice and ethanol coldbath by a liquid nitrogen trap. This removes residual Cl_2 but does not remove the $O_2(^1\Delta_g)$, which can be detected by the faint dimol emission. Under this condition, only dimol emission appears whether or not the Cu coil is heated. We injected some Cl_2 gas downstream from the liquid nitrogen coldtrap but upstream from the heated coil. This caused enhanced red emission. Hence, we conclude that three factors must be present for the production of the strong red emission: $O_2(^1\Delta_g)$ molecules and Cl_2 must both be in contact with the heated metal surface.

If the emitter is formed only on the surface of the coil and then escapes into the gas phase, we might expect the intensity would fall off exponentially with the distance from the coil. We made a crude spatial mapping of the red emission downstream from the coil using the OMA system without the polychromator. We find at low Cl_2 partial pressures in the optical cavity a slight increase of the intensity away from the coil, followed by a slow decrease. These measurements suggest that the reaction responsible for the generation of the strong red emission does not occur exclusively on the metal surface or that some other species generated on the metal surface acts to quench the emitter.

We presently do not know the identity of the emitter but believe it does not contain a metal atom and may contain oxygen and/or chlorine. Clearly, our results demonstrate the importance of Cl_2 in the $O_2(^1\Delta_g)$ feed stream, a conclusion apparently also reached by Zhuang *et al.* [8]. This is in contradiction to the work of Yoshida, Tokuda, and Shimizu [7] who state that unreacted Cl_2 coming from the singlet oxygen generator is not related to the emission they observed. Whatever is the identity of the emitter, it seems that surface-catalyzed reactions are responsible for initiating its creation and that the presence of Cl_2 is necessary as well as $O_2(^1\Delta_g)$. We attempted to increase the partial pressure of Cl_2 by increasing the Cl_2 flow rate through the singlet oxygen generator. As the Cl_2 partial pressure increases in the optical cavity, the intense red emission becomes more localized about the heated coil, suggesting that excess Cl_2 quenches the emitter.

A fuller account of this study has been published [R. Huang, R. Zhang, and R. N. Zare, *Chem. Phys. Lett.* **170** 437–440 (1990)].

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